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Title: Polymer and Additive Mass Spectrometry Literature Review

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Polymer and Additive Mass Spectrometry Literature Review

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U OF O GIP – POLYMER TRACK

Abstract

The use of mass spectrometry in fields related to polymers has increased significantly over the past three decades and will be explored in this literature review. The importance of this technique is highlighted when exploring how polymers degrade, verifying purchased materials, and as internal requirements change. The primary focus will be on four ionization techniques and the triple quadrupole and quadrupole / time-of-flight mass spectrometers. The advantages and limitations of each will also be explored.

Introduction

Since its inception in the early 20th century[1], mass spectrometry (MS) has been an invaluable tool for the scientific community. With its ability to determine elemental composition within a limit of detection reaching the ppm to ppt range[2], it's apparent why polymer scientists would be interested in utilizing this technique.

Mass spectrometry requires gas phase ions to be generated in order for their compositions to be analyzed[3,4]. This would appear to be quite difficult, yet over the years ingenious methods have been developed to suit the purpose of polymer and additive analysis. Primarily it is the ionization method that is altered to have the greatest effect in generating these ions, depending on the sample. This paper will explore the following ionization techniques: matrix-assisted laser desorption/ionization (MALDI), electrospray ionization (ESI), secondary ion mass spectrometry (SIMS), and inductively coupled plasma (ICP). The different types of mass spectrometers will also be briefly discussed.

Current State of the Art

Types of Mass Spectrometers

There are six main types of mass spectrometers that are commercially available[3,4,5], including:

- fourier transform,
- Orbitrap,
- quadrupole-time of flight (Q-ToF),
- triple quadrupole (QQQ),
- time of flight-time of flight (ToF-ToF), and
- ion trap.

The rest of this review will focus on Q-ToF and QQQ instruments, as these are the workhorses of polymer analysis when related to mass spectrometry.

Triple Quadrupole

Quadrupole analyzers utilize four parallel hyperbolic rods that direct current (DC) and/or radio fields (RF) to separate ions based on their mass/charge (m/z) ratio[3-4]. The general scheme of a quadrupole and a QQQ instrument can be seen in Figure 1 & 2.

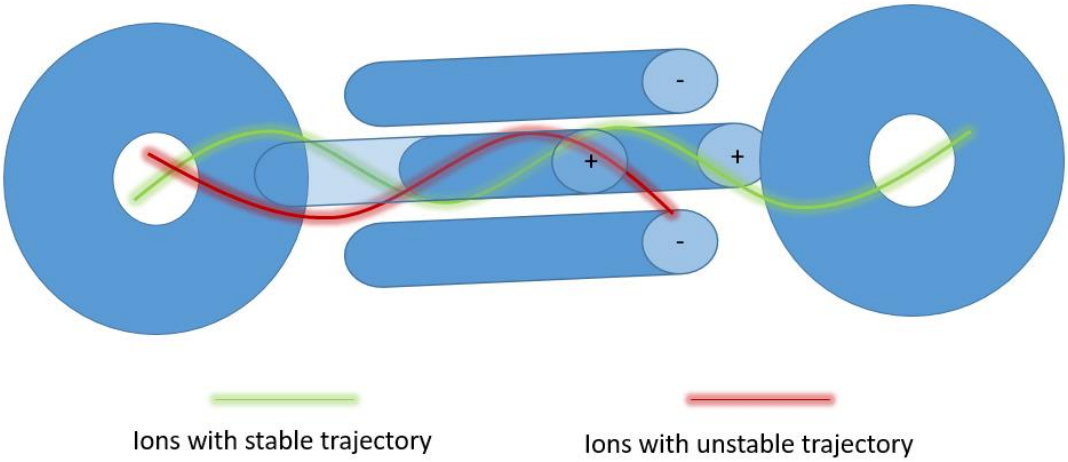

Figure 1: Diagram of a quadrupole used in mass spectrometry. Ions with a selected m/z will have a stable trajectory while all other ions will crash out.

In a QQQ, there are three quadrupoles in sequence, traditionally referred to as Q1, Q2, and Q3. The Q1 is the first mass analyzer where the precursor ion is selected and separated from the rest of the ions in the sample[3],[4]. It is then passed to Q2 which is usually filled with an inert gas and acts as a collision cell[4]. The applied user specified voltage potential is responsible for how fast the precursor ions enter the collision chamber and thus the degree of ion fragmentation. The fragments are then passed to Q3 where DC and RF are utilized to stabilize the trajectory of ions with a specified m/z, passing those ions on to the detector while the ions with an unstable trajectory do not make it to the detector[4]. This type of mass spectrometer is ideal for quantification of chemicals at low mass ranges, such as small molecules, and determining the structure of molecules since it is possible to get enough fragmentation to elute the chemical structure of the sample[4]. However, a QQQ can suffer from resolution issues since it doesn't have large spatial separation of ions and the mass range is generally inferior to the Q-ToF instrument. This leads to the general idea that the QQQ instrument is ideal for targeted analyte analysis.

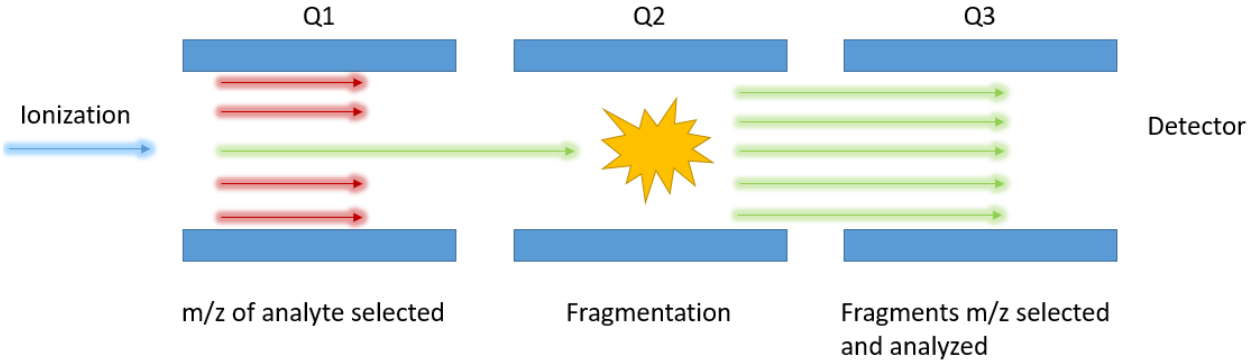

Figure 2: Diagram of a triple quadrupole mass spectrometer. The Q1 area separates the selected m/z parent ion, Q2 is used as a collision cell and Q3 is for further separation of fragmented product ions.

Quadrupole / Time-of-Flight

The Q-ToF (Time-of-Flight) is similar to a QQQ, except that it only uses one quadruple in tandem with ToF. In a Q-ToF, the quadruple allows only the ions of a target m/z to pass through to the collision cell[4]. This cell is usually filled with an inert gas, allowing the sample to fragment and create parent ions. The ions are then passed to the ToF analyzer which uses an electric field, generated by a "pusher", to impart a constant kinetic energy to all ions. The constant kinetic energy causes the lowest m/z ions to reach the detector first, thus increasing spatial separation of ions based on m/z[4]. The design of a Q-ToF instrument is shown in Figure 3. An instrument with a ToF can increase its effective flight time by incorporating a reflectron, further increasing the spatial separation of ions. One of the benefits of a Q-ToF is that it has a very broad range of masses that it can analyze and allows for very high resolution capabilities[4]. This makes Q-ToF ideal when the sample in question has many unknown components and a wide variety of analytes could be present.

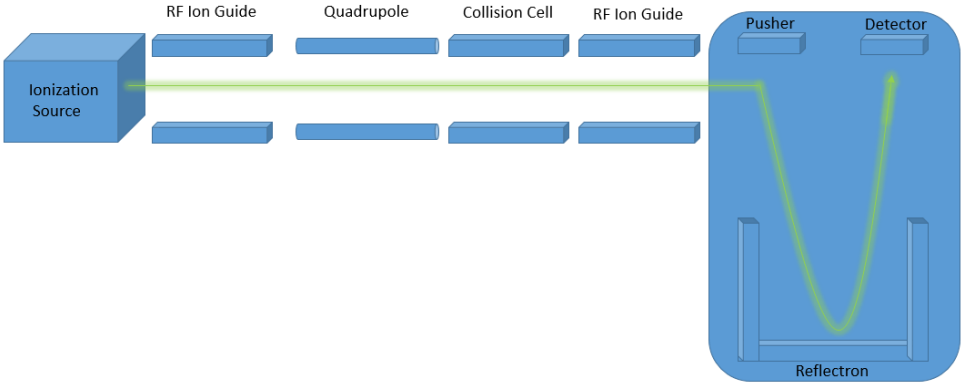

Figure 3: Diagram of a quadrupole / time-of-flight mass spectrometer. This figure shows the use of a reflectron to increase flight time, although this is not required for a Q-ToF instrument.

Ionization Sources

There are four types of ionization sources that will be discussed. They are: MALDI, ESI, SIMS, and ICP-MS. The role of the ionization source is to produce ions in the gas phase, allowing the mass spectrometer to move and detect these ions.

MALDI

MALDI mass spectrometry was developed by Hillenkamp and Karas in 1988[6]. Since then, it has been used to analyze large biomolecules and polymers primarily[6,7,8]. MALDI is a soft ionization process and doesn't cause degradation of polymers, usually producing single charged ions and thus make the analysis of spectra much easier and faster[7,8,9]. Polymer analysis has especially benefited from this ionization method because hard ionization methods tend to degrade polymers during ionization. Additionally, the polymer sample doesn't need to be completely miscible with the matrix, avoiding possible insolubility issues that arise with other ionization sources during sample preparation[5,8].

The process of how MALDI functions is fairly straightforward. First, a matrix is selected to be used with the analyte of choice which is usually a conjugated, aromatic molecule[5,6,7,8]. Once the matrix and analyte are mixed, they are dried in a crystalline like film. The pulsed laser then irradiates the matrix/analyte film, which is absorbed by the matrix causing the analyte to ionize and ablate into the gas phase[6,7,8], which is demonstrated in Figure 4.

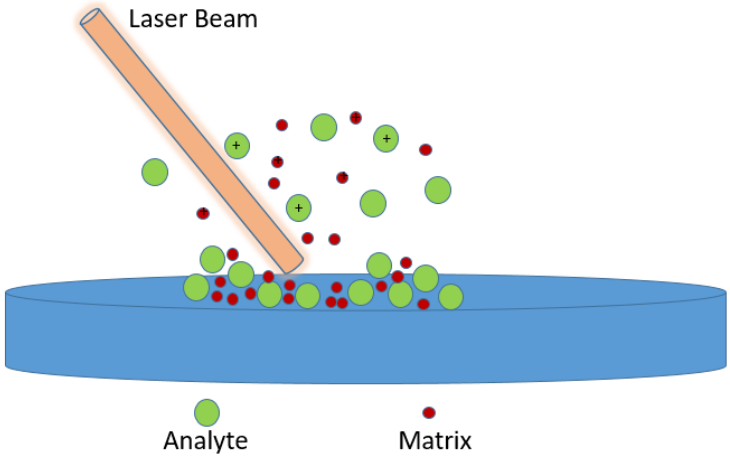

Figure 4: Diagram of the MALDI process. The analyte is ablated and desorbed into the gas phase with a pulsed laser and ions generated by interaction with the matrix.

In order to effectively use MALDI, there are various requirements of the matrix/analyte solution that must be met, including but not limited to; 1) matrix must be able to absorb the laser energy, 2) miscibility of the polymer with the matrix, 3) desorption of analyte by the matrix, and 4) stable in a vacuum[6,7]. While MALDI is great for polymers and oligomers, the presence of the matrix causes low mass molecules (i.e., additives) to be lost in the background and so is only of practical use when analyzing masses over 500 Da[6].

Electrospray Ionization

The use of ESI can also be used in the analysis of polymers due to it also being a soft ionization technique. In ESI, a dilute solution is introduced to a very small capillary needle which has a high voltage applied. The excess charge due to the high potential causes the solution to exit in a Taylor cone, creating a highly charged aerosol[4,5,10]. This excess charge causes the droplets in the aerosol to break apart, eventually into droplets capable of ions that can be analyzed, shown in Figure 5.

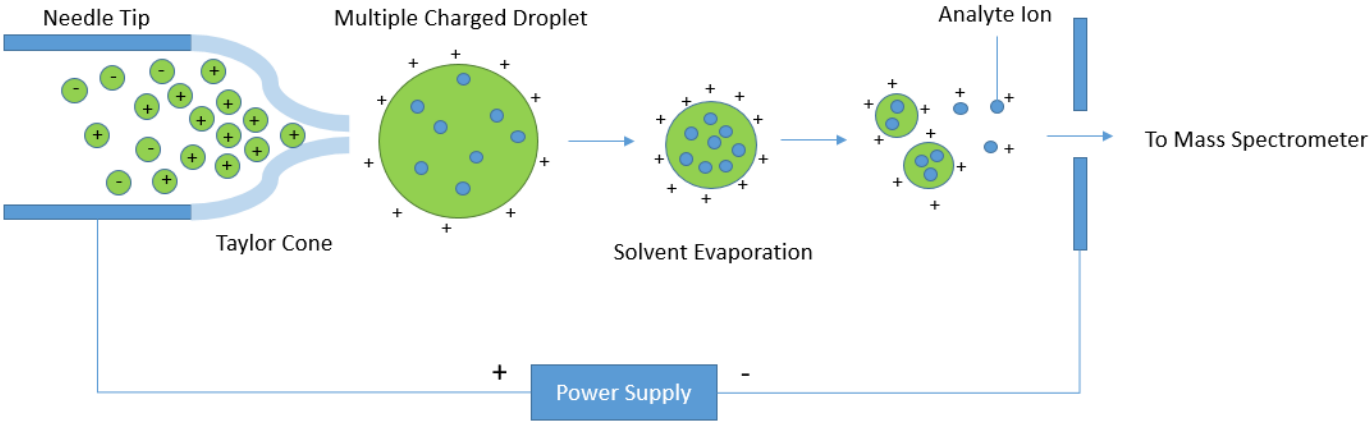

Figure 5: Diagram of the ESI process. As the droplets become smaller, individual analyte ions are produced through coulombic repulsion.

While ESI is an extremely versatile ionization technique, it has two major problems when it comes to polymer analysis. First, it is difficult to find a solvent system that polymers will dissolve in that is also compatible with ESI[4,5,10]. The second issue is that ESI can increase the number of charges on the analyte. This allows high MW materials to be detected on instruments that have a low mass range (such as in a QQQ instrument). However, when the multiple charges are applied to polymers, this causes the spectra to become extremely complex and difficult to analyze.

When looking at small molecule analysis, such as for additives and contaminants, ESI is a great technique. Not only does the soft ionization cause very little fragmentation in the source, but the ability to get multiple charged species can be used to identify larger molecules[5,10]. The knowledge required to run ESI is also fairly low, allowing it to be very user friendly as well.

Secondary Ion Mass Spectrometry

SIMS is a technique that typically uses Ar, Xe, Ga, or Cs as a primary ion beam[5,11]. This beam is focused and accelerated onto the sample surface causing an ejection of secondary ions, including other atomic and molecular species that aren't of interest[5,11]. The ionized analytes are then accelerated into the mass spectrometer using a focusing lens. This technique is demonstrated in Figure 6. Since the primary ion beam is only able to penetrate 1 to 2 nm into the surface, thus this is a surface analysis technique only.

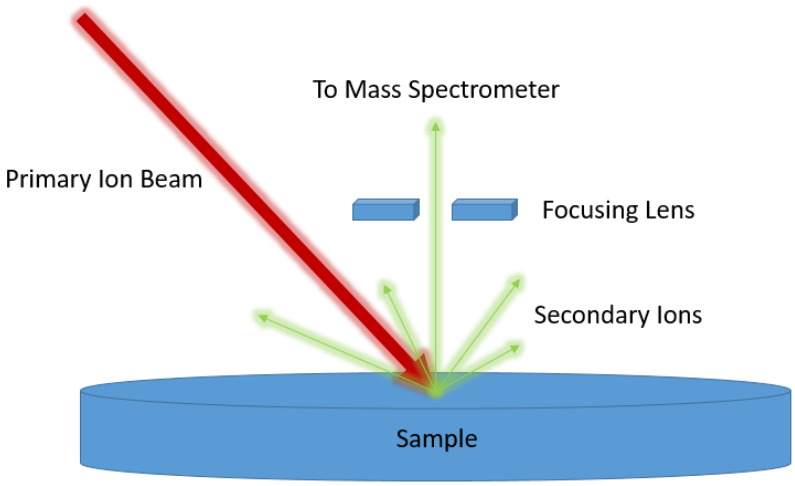

Figure 6: Diagram of the SIMS process. The primary ion beam impacts the sample surface, causing secondary ions to be released.

Since SIMS is limited to the surface, it is often used to determine surface contaminants in polymers, as well as end group, chemical, and repeat unit analysis[5,11]. It is also good for polymers that can't be analyzed in any other way due to insolubility issues. Small molecule analysis is generally not performed using SIMS.

Inductively Coupled Plasma Mass Spectrometry

ICP-MS is a technique that uses an oscillating radio and magnetic field to produce an Ar plasma that can reach temperatures above 10,000 ˚K, completely destroying any sample that is introduced. Once the sample is destroyed, the individual atoms (now ionized) are directed into the mass spectrometer, which is capable of ppt concentrations[2]. Figure 7 demonstrates this technique.

Due to the highly destructive nature of ICP-MS, this method is usually limited to determining contamination within polymers[2]. For example, tin (II) 2-ethylhexanoate, used as a polymerization catalyst, remains within the polymer after polymerization. Understanding how much remains and how it continues to affect the polymer years after formulation could be investigated by ICP-MS. This ionization method would be used over others in this case due to its extremely high sensitivity and the ability to remove all tin from the polymer matrix.

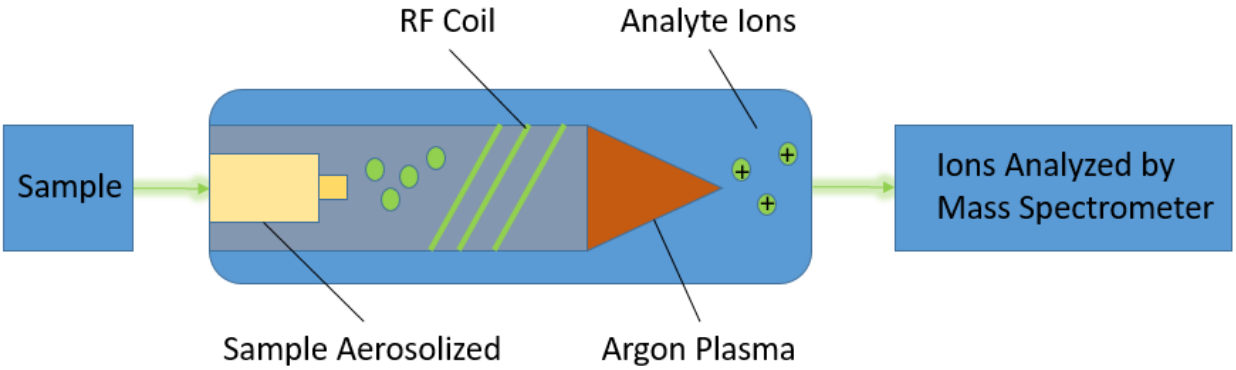

Figure 7: Diagram of ICP-MS. Aerosolized sample enters the argon plasma, causing complete destruction of the sample and producing ions.

Conclusions

During my time at LANL, I've seen the potential application that could be used on polymers used at MST-7. Many studies performed are related to the ageing of polymers and how they degrade or change over time, whether it be due to time, heat, or radiation. Using mass spectrometry, it would be possible to see exactly how these polymers are changing, including but not limited to their chemical composition, oligomer distribution, M_w, and M_n. It would also be valuable in understanding how additives that are used in these polymer makeups are aging and what metabolites may be present under different types of aging. Additionally, if vendor polymer formulations change, this can have major implications in the design and application of various materials. The ability to verify that the composition of the polymer being procured is what's expected is another very beneficial use of mass spectrometry to MST-7.

Mass spectrometry is an extremely powerful tool and can elute composition of polymers and their additives, such as M_w, M_n, chemical composition, copolymer analysis or end group analysis. While not every ionization technique is capable of all type of analyses, through a multi-faceted approach it's possible to determine these various characteristics of polymers and additives with extreme accuracy.

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